

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 11/10, G02B 6/44	A1	(11) International Publication Number: WO 99/61535 (43) International Publication Date: 2 December 1999 (02.12.99)
(21) International Application Number: PCT/NL99/00321 (22) International Filing Date: 21 May 1999 (21.05.99) (30) Priority Data: 09/084,918 28 May 1998 (28.05.98) US (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): MURPHY, Edward, Joseph [US/US]; 742 South Mitchel, Arlington Heights, IL 60005 (US). CLASSEY, Jeffrey, Lee [US/US]; 296 Crosscut Drive, Denver, NC 28037 (US). SZUM, David, Michael [US/US]; 646 North Oaklawn, Elmhurst, IL 60126 (US). (74) Agent: DEN HARTOG, Jeroen, Hendrikus, Joseph; Octrooibu- reau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: RADIATION-CURABLE INK COMPOSITION FOR COATED OPTICAL GLASS FIBERS (57) Abstract Provided is a radiation-curable ink composition containing a radiation-curable carrier system containing at least one radiation-curable monomer or oligomer and at least one pigment dispersed in the radiation-curable carrier system in an amount sufficient to provide a color which is visible without magnification. The pigment is substantially insoluble in the radiation-curable carrier system whereby the particulate shape of the pigment is substantially retained in the radiation-curable carrier system, the pigment having a particle size that substantially avoids pigment induced microbending of an optical glass fiber coated with the ink coating.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

RADIATION-CURABLE INK COMPOSITION FOR COATED OPTICAL GLASS
FIBERS

5

1. Field of Invention

The invention relates to a method for making radiation-curable ink composition, radiation-curable ink composition and a ribbon assembly.

10

2. Background of the Invention

Optical glass fibers are usually coated with two superposed radiation-cured coatings, which together form a primary coating. The coating which contacts the glass surface is called the inner primary coating and the
15 overlaying coating is called the outer primary coating.

The inner primary coating is usually a soft coating having a low glass transition temperature (hereinafter "Tg"), to provide resistance to microbending. Microbending can lead to attenuation of the signal
20 transmission capability of the coated optical glass fiber and is therefore undesirable. The outer primary coating is typically a harder coating providing desired resistance to handling forces, such as those encountered when the coated
25 fiber is cabled.

For the purpose of multi-channel transmission, optical glass fiber assemblies containing a plurality of coated optical fibers have been used. Examples of optical glass fiber assemblies include ribbon assemblies and
30 cables. A typical optical glass fiber assembly is made of

a plurality of coated optical glass fibers which are bonded together in a matrix material. For example, the matrix material can encase the optical glass fibers, or the matrix material can edge-bond the optical glass fibers
5 together.

Optical glass fiber assemblies provide a modular design which simplifies the construction, installation and maintenance of optical glass fibers by eliminating the need to handle individual optical glass
10 fibers.

Coated optical glass fibers for use in optical glass fiber assemblies are usually coated with an outer colored layer, called an ink coating, or alternatively a colorant is added to the outer primary coating to
15 facilitate identification of the individual coated optical glass fibers. Thus, the matrix material which binds the coated optical glass fibers together contacts the outer ink layer if present, or the colored outer primary coating.

20 When a single optical glass fiber of the assembly is to be fusion connected with another optical glass fiber or with a connector, an end part of the matrix layer can be removed to separate each of the optical glass fibers.

25 Desirably, the primary coatings on the coated optical glass fibers, and the ink coating if present, are removed simultaneously with the matrix material to provide bare portions on the surface of the optical glass fibers

(hereinafter referred to as "ribbon stripping"). In ribbon stripping, the matrix material, primary coatings, and ink coating, are desirably removed as a cohesive unit to provide a clean, bare optical glass fiber which is
5 substantially free of residue.

Ink coatings usually have a thickness of about 3 to about 10 microns and are formed from a pigment dispersed within a UV curable carrier system. The UV curable carrier system contains a UV curable oligomer or
10 monomer that is liquid before curing to facilitate application of the ink composition to the optical glass fiber, and then a solid after being exposed to UV radiation. In this manner, the UV curable ink composition can be applied to a coated optical glass fiber in the same
15 manner as the inner primary and outer primary coatings are applied.

Modern high speed optical glass fiber drawing towers operate at a very high speed. Thus, the ink composition must have a very fast cure speed to ensure
20 complete cure of the ink coating on the high speed drawing tower. However, the increase in cure speed should not come at the expense of other important properties of the ink coating, such as providing suitable break out performance. In addition, ink compositions should not contain
25 ingredients that can migrate to the surface of the optical glass fiber and cause corrosion. The ink composition should also not contain ingredients which can cause instability in the protective coatings or matrix material. Ink coatings for optical glass fibers should be color fast

for decades, not cause attenuation of the signal transmission, be impervious to cabling gels and chemicals, and allow sufficient light penetration for fiber core alignment.

5 From the above, it is clear that optical glass fiber technology places many unique demands on radiation-curable ink compositions which more conventional technologies, such as printing inks, do not.

 U.S. patent No. 4,629,285 discloses a method
10 for making an ink coating on a coated optical glass fiber in which a UV curable ink is applied to a coated optical glass fiber. The ink coating is applied in a method that preserves the concentricity of the optical glass fibers. The preferred inks are pigmented semi-opaque UV curable
15 polymeric inks. However, the ink compositions disclosed in this patent do not have a sufficiently fast enough cure speed to be used on modern high speed optical glass fiber drawing and coating towers.

 Laid open Japanese Patent Application No. H1-
20 191475 discloses a radiation-curable ink composition containing an organic polysiloxane compound. The polysiloxane compound provides the ink coating with the ability to separate more easily from the matrix material in a unit assembly.

25 Published Japanese Patent Application No. 64-22970 discloses radiation-curable ink compositions containing specific radiation-curable oligomers. The ink composition provides an ink coating having adhesion to the outer primary coating which is separable from the matrix

material in a ribbon assembly.

Conventional ink coatings can have problems with concentricity. If the ink coating is not concentric, undesirable attenuation of the signal transmission may occur. Thus, there is a need for an ink composition that can be applied to a coated optical glass fiber in a concentric layer.

Ink compositions containing pigments can be very difficult to suitably cure via exposure to actinic radiation. The pigments can cause an undesirable reduction in cure speed. Thus, there is a need for a fast curing ink composition that can be used on high speed modern day optical glass fiber drawing and coating towers.

Ink coatings can have a non-uniform coloring. Therefore, there is a need for an ink composition that is capable of providing an ink coating having a uniform color.

There is also a need for an ink composition that provides an ink coating which is significantly less susceptible to causing microbending in an optical glass fiber that can lead to undesirable attenuation of the signal transmission.

SUMMARY OF THE INVENTION

25

An objective of the present invention is to provide an ink composition which when coated and cured on coated optical glass fibers provides an ink coating having a uniform color and which is significantly less

susceptible to causing microbending in the optical glass fiber.

A further objective is to provide a method for making an ink composition which when coated and cured on
5 coated optical glass fibers provides an ink coating having a uniform color and which is significantly less susceptible to causing microbending in the optical glass fiber.

The above objectives and other objects can be
10 obtained by the following. Provided is a novel radiation-curable ink composition which when coated and suitably cured at a coating thickness of 3-10 μm thickness on a coated optical glass fiber provides an ink coating having a substantially uniform color, the improved ink
15 composition comprising:

a radiation-curable carrier system containing at least one radiation-curable monomer or oligomer; and
at least one pigment dispersed in the radiation-curable carrier system in an amount sufficient
20 to provide a color which is visible without magnification, the pigment being substantially insoluble in the radiation-curable carrier system whereby the particulate shape of the pigment is substantially retained in the radiation-curable carrier system, and wherein said pigment
25 contains about 230 or less particles having a size of about 3 microns or greater per one square centimeter of cured ink coating.

Also provided is a novel method of making an

improved radiation-curable ink composition which when coated and suitably cured on a coated optical glass fiber provides an ink coating having a substantially uniform color, the method comprising the steps of:

- 5 combining a radiation-curable carrier system containing at least one radiation-curable monomer or oligomer with at least one pigment to provide an ink composition, wherein the pigment is present in an amount sufficient to provide a color which is visible without
10 magnification, the pigment being substantially insoluble in the radiation-curable carrier system whereby the particulate shape of the pigment is substantially retained in the radiation-curable carrier system;

- filtering the ink composition to selectively
15 remove pigment particles having a size of about 3 microns or greater to substantially avoid pigment induced microbending of an optical glass fiber coated with the ink coating. Also provided is a ribbon assembly containing at least one optical glass fiber coated with an ink coating
20 according to the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

- The ink composition of this invention can be
25 based on the radiation-curable carrier system of any known ink composition for coating and identifying coated optical glass fibers, which contains monomers or oligomers that are radiation curable. Commercial examples of suitable radiation-curable carriers include the radiation-curable

carriers utilized in the Cablelite series of UV curable inks from DSM Desotech Incorporated which are based on multi-functional acrylate monomers.

Ink coatings are usually about 3 to about 10
5 microns thick and are usually concentric to prevent attenuation of the signal transmission. However, if desired, the ink coating can be applied in any form suitable to provide visible color identification of the individual coated optical glass fibers. Examples of
10 suitable coatings include dashes, dots, lines, and rings. Preferably, the ink coating is substantially concentric. The ink coating compositions according to the present invention are capable of providing substantially concentric ink coatings, as well as discontinuous coatings
15 such as dashes, dots, lines, and rings.

The ink coatings generally have a Tg of at least about 30°C , more preferably at least about 50°C. One of ordinary skill in the art of formulating radiation-curable ink compositions knows how to adjust the
20 radiation-curable composition to provide the desired properties of the cured coating. Thus, radiation-curable compositions which are usually used for forming outer primary coating compositions can be reformulated and utilized as the radiation-curable carrier system in the
25 ink composition according to the present invention. Examples of suitable radiation-curable compositions which may be reformulated variously include those which are disclosed in U.S. patent numbers 4,624,994; 4,682,851; 4,782,129; 4,794,133; 4,806,574; 4,849,462; 5,219,896; and

5,336,563.

Radiation-curable carriers which are suitable for forming the present ink composition contain one or more radiation-curable oligomers or monomers having at least one functional group capable of polymerization when exposed to actinic radiation. Suitable radiation-curable oligomers or monomers are now well known and within the skill of the art.

Commonly, the radiation-curable functionality used is ethylenic unsaturation, which can be polymerized through radical polymerization or cationic polymerization. Specific examples of suitable ethylenic unsaturation are groups containing acrylate, methacrylate, styrene, vinyl ether, vinyl ester, N-substituted acrylamide, -vinyl amide, maleate esters, and fumarate esters. Preferably, the ethylenic unsaturation is provided by a group containing acrylate, methacrylate, or styrene functionality.

Another type of functionality generally used is provided by, for example, epoxy groups, or thiol-ene or amine-ene systems. Epoxy groups can be polymerized through cationic polymerization, whereas the thiol-ene and amine-ene systems are usually polymerized through radical polymerization. The epoxy groups can be, for example, homopolymerized. In the thiol-ene and amine-ene systems, for example, polymerization can occur between a group containing allylic unsaturation and a group containing a tertiary amine or thiol.

Preferably, at least about 80 mole %, more

preferably, at least about 90%, and most preferably substantially all of the radiation-curable functional groups present in the oligomer are acrylate or methacrylate. The remainder, if any, preferably is N-vinyl
5 and/or (meth)acrylamide functional.

A mixture of mono-, di-, tri-, tetra-, and higher functionalized oligomers can be used to achieve the desired balance of properties, wherein the functionalization refers to the number of radiation-
10 curable functional groups present in the oligomer.

The oligomers usually comprise a carbon-containing backbone structure to which the radiation-curable functional group(s) are bound. Examples of suitable carbon-containing backbones include polyethers,
15 polyolefins, polyesters, polyamides, and polycarbonates. The size of the carbon-containing backbone can be selected to provide the desired molecular weight. The number average molecular weight of the oligomer is usually between about 500 to about 10,000, preferably between
20 about 500 to about 7,000, and most preferably between about 1,000 to about 5,000.

For example, the carbon-containing backbone of the oligomer can comprise aromatic groups and ring-opened epoxy groups or alkoxy groups. The oligomer can be
25 represented by, for example:

R-Ar-R; or

R-L-Ar-L-R

where r is a radiation-curable functional group,

Ar is an aromatic group containing moiety, and L is a linking group.

5 Examples of suitable linking groups include alkoxy or ring opened epoxy such as ethoxy, propoxy, butoxy, and repeat units thereof. L can also be a urethane or urea linking group.

 The aromatic groups can be, for example,
10 derived from bisphenol units, such as bisphenol A. A preferred oligomer is a diglycidyl ether derivative of bisphenol A to which acrylate functional groups have been bound. A commercially available example of such an oligomer is CN-120 (Sartomer), which has a molecular
15 weight of about 1300, and when cured has a Tg of about 65°C .

 Another example of a preferred oligomer is a trifunctional polyether or polyester having a molecular weight of about 500 to about 5000. A preferred example of
20 a trifunctional oligomer is the commercially available polyurethane triacrylate Ebecryl 264, which has a molecular weight of about 2000 and when cured a Tg of about 42°C.

 The radiation-curable carrier systems may also
25 contain a reactive diluent which is used to adjust the viscosity. The reactive diluent can be a low viscosity monomer containing having at least one functional group capable of polymerization when exposed to actinic radiation. This functional group may be of the same nature

as that used in the radiation-curable monomer or oligomer. Preferably, the functional group present in the reactive diluent is capable of copolymerizing with the radiation-curable functional group present on the radiation-curable monomer or oligomer.

For example, the reactive diluent can be a monomer or mixture of monomers having an acrylate or vinyl ether functionality and an C_4 - C_{20} alkyl or polyether moiety. Particular examples of such reactive diluents include: hexylacrylate, 2-ethylhexylacrylate, isobornylacrylate, decyl-acrylate, laurylacrylate, stearylacrylate, 2-ethoxyethoxy-ethylacrylate, laurylvinylether, 2-ethylhexylvinyl ether, N-vinyl formamide, isodecyl acrylate, isooctyl acrylate, N-vinyl-caprolactam, N-vinylpyrrolidone, and the like.

Another type of reactive diluent that can be used is a compound having an aromatic group. Particular examples of reactive diluents having an aromatic group include: ethyleneglycolphenylether-acrylate, polyethyleneglycolphenyletheracrylate, polypropyleneglycolphenylether-acrylate, and alkyl-substituted phenyl derivatives of the above monomers, such as polyethyleneglycolnonylphenyl-etheracrylate.

The reactive diluent can also comprise a diluent having two or more functional groups capable of polymerization. Particular examples of such monomers include: C_2 - C_{18} hydrocarbon-dioldiacrylates, C_4 - C_{18} hydrocarbondivinylethers, C_3 - C_{18} hydrocarbon triacrylates, and the polyether analogues thereof, and the like,

such as 1,6-hexanedioldiacrylate, trimethylolpropanetri-
acrylate, hexanedioldivinylether, triethylene-
glycoldiacrylate, pentaerythritol-triacrylate,
ethoxylated bisphenol-A diacrylate, and tripropyleneglycol
5 diacrylate.

If the radiation-curable functional group of
the radiation-curable monomer or oligomer is an epoxy
group, for example, one or more of the following compounds
can be used as the reactive diluent:

10 epoxy-cyclohexane, phenylepoxyethane, 1,2-epoxy-4-
vinylcyclohexane, glycidylacrylate, 1,2-epoxy-4-
epoxyethyl-cyclohexane, diglycidylether of polyethylene-
glycol, diglycidylether of bisphenol-A,
and the like.

15 If the radiation-curable functional group of
the radiation-curable monomer or oligomer has an amine-ene
or thiol-ene system, examples of reactive diluents having
allylic unsaturation that can be used include:

diallylphthalate, triallyltri-mellitate,
20 triallylcyanurate, triallylisocyanurate, and
diallylisophthalate.

For amine-ene systems, amine functional diluents that can
be used include, for example:

the adduct of trimethylolpropane, isophorondiisocyanate
25 and di(m)ethylethanolamine, the adduct of hexanediol,
isophoron-diisocyanate and dipropylethanolamine, and
the adduct of trimethylol propane, tri-
methylhexamethylenediisocyanate and
di(m)ethylethanolamine.

Other additives which can be used in the ink coating composition include, but are not limited to, photoinitiators, catalysts, lubricants, wetting agents, antioxidants and stabilizers. The selection and use of
5 such additives is within the skill of the art.

Furthermore, the ink composition can contain at least one additive component which facilitates breakout performance. For example, the additive can be a hydrophobic polymer or oligomer, such as a silicone
10 compound or a radiation-curable silicone compound. The amount of this additive can be that which is effective to retain suitable adhesion of the ink coating to the coated optical glass fiber but which provides suitable breakout characteristics between the ink coating and the matrix
15 material of a ribbon assembly.

Conventional inorganic and organic pigments which have been processed in accordance with the present invention can be used to formulate the improved radiation-curable ink composition according to the present
20 invention. The use of the term "pigment" refers to both inorganic and organic pigments. The pigments are substantially insoluble in the radiation-curable carrier system whereby the particle shape of pigment is substantially retained in the ink composition. Soluble
25 pigments can be combined with the insoluble pigments if desired. However, use of soluble pigments is not preferred because they can undesirably affect the properties of the ink coating. Therefore, preferably the ink composition is substantially free of pigments which are substantially

soluble in the radiation-curable carrier system.

Ink compositions for application on a glass optical glass fiber drawing tower usually must pass through a die for applying the ink composition to the coated optical glass fiber. The die has a diameter which provides the desired thickness of the ink coating to be applied to the coated optical glass fiber. For example, if an ink coating having a thickness of 5 microns is desired, the diameter of the die should be 10 microns greater than the diameter of the coated optical glass fiber passing through the die.

It has now been found that pigment particles having a size about, or greater than the thickness of the ink coating can cause microbending in the optical glass fiber which can lead to undesirable attenuation of the signal transmission through the optical glass fiber. It is believed that when a matrix material is applied to the coated optical glass fiber for forming a ribbon assembly, the matrix material exerts a force on the pigment particles. This force can be transmitted through the pigment particle and protective coatings to the surface of the optical glass fiber, thereby causing microbending in the optical glass fiber.

Based on experimentation, it has been found that the ink composition should be formulated to provide as few pigment particles as possible having a size of at least the thickness of the ink coating to avoid pigment particle induced microbending. However, it is unexpected that a certain amount of relatively large particles can be

acceptable. Suitable amounts of pigment particles having a size equal to or greater than the thickness of the ink coating have been found to be about 230 or less, preferably about 200 or less, more preferably about 150 or less, and most preferably about 100 or less pigment particles per square centimeter of ink coating. Thus, for ink coatings having a thickness of about 3 to about 10 microns, the quantity of pigment particles having a size of about 3 microns and greater should be about 230 or less, preferably about 200 or less, more preferably about 150 or less, and most preferably about 100 or less per square centimeter of ink coating.

Even though it is preferred to have no particles with a size of about 3 micron and greater, it appears to be acceptable to have 5 particles or more per square centimeter of ink coating.

The pigment particles in the ink coating preferably have a number average mean particle diameter of about 0.8 microns or less, more preferably from about 0.1 to about 0.8 microns.

In general, pigment manufacturers can manufacture pigments having the desired particle size according to the request of customers. However, such pigments are usually produced for use in a wide variety of applications in which pigment induced microbending is not a factor. Therefore, these pigments generally contain an undesirable number of particles having a size of 3 microns or greater. To reduce the number of undesirable particles, the pigment can be suitably dispersed in at least a

portion of the desired amount of radiation-curable carrier and then processed according to the present invention to provide the desired particle size. The ink composition can be processed according to the present invention by

5 subjecting the ink composition to a filtering process to selectively remove undesirable pigment particles, such as those particles having a size of at least about the desired ink coating thickness. For example, if the ink composition is to be applied at a thickness of about 3 to

10 about 10 microns, pigment particles having a size of about 3 microns and greater can be selectively removed via filtering to the extent that about 230 or less, preferably about 200 or less, more preferably about 150 or less, and most preferably about 100 or less per square centimeter

15 remain.

The filtering process can be carried out by passing the ink composition through a suitable filter under prevailing atmospheric pressure or at increased pressures. The use of filters is now well known in the

20 art. Based on the disclosure provided herein, the selection of the filter should be such that undesirable pigment particles having a size of about 3 microns and greater are selectively removed to substantially reduce pigment particle induced microbending in ribbon

25 assemblies. However, significant amounts of pigment particles having a size below about 3 microns should not be removed to avoid color degradation.

If desired, the pigment can be suitably dispersed in one or more of the components of the

radiation-curable carrier system and then processed. The remaining components of the radiation-curable carrier system can then be combined with the processed pigment. For example, to facilitate quicker and simpler filtering, the pigment can be suitably dispersed in a low viscosity diluent and then subjected to processing. After which, the remaining components, such as oligomers or monomers, can be combined with the processed pigment to form the ink composition.

10 Ribbon assemblies utilizing 12 or less coated optical glass fibers require only 12 colors to adequately distinguish each of the coated optical fibers from one another. However, in larger ribbon assemblies, more than 12 colors may be utilized to adequately distinguish the coated optical glass fibers from one another. Any color
15 may be used in the ink composition according to the present invention. Examples of twelve colors normally used for making ribbon assemblies include: black, white, yellow, blue, red, green, orange, brown, pink, aqua, violet and gray.

A specific example of a suitable black pigment includes carbon black.

A specific example of a suitable white pigment includes titanium dioxide.

25 Specific examples of suitable yellow pigments include diarylide yellow and diazo based pigments.

Specific examples of suitable blue pigments include phthalocyanine blue, basic dye pigments, and phthalocyanines.

Specific examples of suitable red pigments include anthraquinone (red), naphthole red, monoazo based pigments, quinacridone pigments, anthraquinone, and perylenes.

5 Specific examples of suitable green pigments include phthalocyanine green and nitroso based pigments.

Specific examples of suitable orange pigments include monoazo and diazo based pigments, quinacridone pigments, anthraquinones and perylenes.

10 Specific examples of suitable violet pigments include quinacrinode violet, basic dye pigments and carbazole dioxazine based pigments.

Suitable aqua, brown, gray, and pink pigments can easily be formulated by combining other colors. One
15 skilled in the art is able to form any color as desired by combining different.

The pigment can be present in the ink composition in an amount that provides coloration that is visible without magnification to facilitate identification
20 of the individual colored optical glass fiber. The amount of the pigment should not be so great as to significantly reduce the cure speed of the ink composition or result in other undesirable affects. Examples of suitable amounts of pigment have been found to be from about 1 to about 20
25 weight %, preferably about 1 to about 15 weight %, more preferably about 1 to about 10 weight %, based on the total weight of the ink composition.

A suitable ink composition comprises:

about 1 to about 20 weight % of at least one

pigment, wherein the quantity of pigment particles having a size of about 3 microns or greater is about 230 or less per square centimeter of ink coating; and

5 about 80 to about 99% of a radiation-curable carrier system.

A preferred ink composition comprises:

about 1 to about 20 weight % of at least one pigment, wherein the quantity of pigment particles having a size of about 3 microns or greater is about 200 or less
10 per square centimeter of ink coating;

about 20 to about 80 weight % of at least one radiation-curable oligomer;

about 5 to about 80 weight % of at least one radiation-curable diluent monomer; and

15 about .1 to about 20 weight % of at least one photoinitiator, based on the total weight % of the ink composition.

The ink coating composition can be applied to the coated optical glass and cured using any suitable
20 method. An example of a suitable method is disclosed in U.S. patent No. 4,629,285, the complete disclosure of which is incorporated herein by reference. The ink composition can also be applied in a manner similar to the application of the outer primary coating on an optical
25 glass fiber drawing and coating tower.

Ribbon assemblies are now well known in the art and one skilled in the art will easily be able to use the disclosure provided herein to prepare a novel ribbon assembly containing at least one of the improved ink

coated optical glass fibers for the desired applications. The novel ribbon assembly made according to this invention can be used in telecommunication systems. Such telecommunication systems typically include ribbon
5 assemblies containing optical glass fibers, transmitters, receivers, and switches. The ribbon assembly containing the coated optical glass fibers are the fundamental connecting units of telecommunication systems. The ribbon assembly can be buried under ground or water for long
10 distance connections, such as between cities. The ribbon assembly can also be used to connect directly to residential homes.

The novel ribbon assembly made according to this invention can also be used in cable television
15 systems. Such cable television systems typically include ribbon assemblies containing optical glass fibers, transmitters, receivers, and switches. The ribbon assembly containing the coated optical glass fibers are the fundamental connecting units of such cable television
20 systems. The ribbon assembly can be buried under ground or water for long distance connections, such as between cities. The ribbon assembly can also be used to connect directly to residential homes.

The invention will be further explained by the
25 following non-limiting examples.

Examples and Comparative Examples

Commercially available inks were filtered using the following three different filter units: (1)

Millipore CRO1 filter, (2) Millipore CRO1 filter in series with a Pall Ultipleat 4.5 and (3) CRK3 filter. The quantity of pigment particles in each sample having a size of 3 microns and greater was then determined as follows.

5 3 inch by 1 inch microscope slides were cleaned using ethanol and lint free cotton wipes. Three 0.011 gram (+/- 0.003 grams) samples of each filtered ink were taken using glass capillary droppers and applied to the cleaned slides. A cover slip was placed over each
10 sample and pressure was applied to edges of the cover slip to provide samples having a diameter between 9 and 12 mm. The thickness of the sample coating being tested is usually from about 40 to about 80 microns thick, depending upon the viscosity of the ink coating composition and the
15 pressure applied to the cover slip. The samples were covered prior to exposure to UV light to prevent curing by the overhead lighting. Each sample was then cured by exposure to a 1.0 J/cm² dose of UV light from a fusion D Lamp under a nitrogen atmosphere.

20 The number of particles having a size of 3 microns or greater per square centimeter for each sample was determined using ASTM E20-85 and ASTM D1366-86, as follows. A sample area of 4 mm² was sectioned off using a pen for viewing under a microscope. The microscope was
25 calibrated within 24 hours of preparing the slides, as described below. A file containing a photograph of a ruler was retrieved and the units were set to microns. A line was made from the first large slash mark to the last large slash mark, which equals 100 microns. The sample slides

were examined under 400x magnification. Each slide was scanned to locate one corner of the marked off area in which to begin counting. Particles having a size of 3 microns and greater were counted. Once a particle was
5 identified, a photograph of the image was captured on the computer. A line was made from end to end of the particle and measured. Examination of the slide for particles was kept within the square of 4 mm². Each sample area of 4 mm² was divided into 12 computer monitor screens per row and
10 12 computer monitor screens per column. If the particle count exceeded 10 particles per computer monitor screen, a particle count was done on only one screen and multiplied by 144 screens to arrive at the number of particles per 4 mm². If the particle count exceeded 10 particles per
15 column or per row, a particle count was only done on the row or column and multiplied by 12 to arrive at the number of particles per 4 mm². The average number of particles for the three samples was determined and then converted to average number of particles per cm². The results are shown
20 in Table 1.

The microscope was calibrated as follows. A micrometer from American Optical Company having a length of 2 mm, divided into units of 0.01 mm (10 microns) was imaged by the microscope using the 40x objective. This
25 image was received by the video camera and sent to the video monitor. The image on the video monitor was then transferred to the computer using the digital imaging system and was viewed on the computer monitor. A section of this image equal to 200 microns on the micrometer is

utilized for the purpose of spatial calibration in the computer imaging system. The software (Optimas) provides a cue for a new calibration, at which point a straight line is drawn with a mouse across the section of the micrometer image being used for the calibration. The software then asks for the length of this line. Since the micrometer is 200 microns, the length of 200 microns is inputted into the computer. This information provides the basis for the software to make size determinations of particles or other objects imaged by the microscope.

Once the software has been calibrated, an image of the system of interest is sent to the computer from the microscope. Once any particles or objects are identified and selected for measurement, a line is drawn across the object using the mouse. Based upon the spatial calibration information which the software has in memory, the distance of the line, and therefore the size of the object, is displayed on the monitor. The calibration of the software was conducted every time the software was re-opened, and the microscope objective used for the calibration and the subsequent particle measure were the same.

Table 1

Ink		Control	CRO1	Ultipleat	CRK3
Green	Ave. No. Part. ≥ 3 F / cm ²	392	642	25	0
	Ave. No. Part. ≥ 3 F sample	15.67	25.67	1.00	0
Aqua	Ave. No. Part. ≥ 3 F / cm ²	233	258	125	0
	Ave. No. Part. ≥ 3 F sample	9.33	10.33	5.00	0
Blue	Ave. No. Part. ≥ 3 F / cm ²	1,267	1,833	200	17
	Ave. No. Part. ≥ 3 F sample	50.67	73.33	8.00	0.67
Violet	Ave. No. Part. ≥ 3 F / cm ²	12,700	708	8	8
	Ave. No. Part. ≥ 3 F sample	508.00	28.33	0.33	0.33
Brown	Ave. No. Part. ≥ 3 F / cm ²	182,400	12,500	75	67
	Ave. No. Part. ≥ 3 F sample	7,296.00	500.00	3.00	2.67
Red	Ave. No. Part. ≥ 3 F / cm ²	5,600	267	58	8
	Ave. No. Part. ≥ 3 F sample	224.00	10.67	2.33	0.33

Since the ink coating thickness used to generate the test results shown in Table 1 were significantly greater than the usual thickness of an ink coating on an optical glass fiber, the number of pigment particles per square centimeter having a size greater than 3 microns should be significantly less for the examples when measured at the usual ink coating thickness of 3 to 10 microns.

Thus, the number of particles preferably is measured at the actual ink-coating thickness. However, it is also possible to measure the number of particles at e.g. 40 micron, and calculate the number in an actual coating of e.g. 3, 5 or 10 micron.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to those of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

CLAIMS

1. Radiation-curable ink composition which when coated
and suitably cured at a coating thickness from about
5 3 to about 10 microns on a coated optical glass
fiber provides an ink coating having a substantially
uniform color, the ink composition comprising:
a radiation-curable carrier system containing at
least one radiation-curable monomer or oligomer; and
10 at least one pigment dispersed in said radiation-
curable carrier system in an amount sufficient to
provide a color which is visible without
magnification, said pigment being substantially
insoluble in said radiation-curable carrier system
15 whereby the particulate shape of said pigment is
substantially retained in said radiation-curable
carrier system, and wherein said pigment contains
about 230 or less particles having a size of about 3
microns or greater per one square centimeter of
20 cured ink coating.
2. A radiation-curable ink composition according to
claim 1, wherein said pigment having a number
average mean particle diameter of less than about
0.5 microns.
- 25 3. A radiation-curable ink composition according to any
one of claims 1-2, wherein said pigment contains
about 200 or less particles having a size of about 3
microns or greater per one square centimeter of
cured ink coating.

4. A radiation-curable ink composition according to claim 3, wherein said pigment contains about 100 or less particles having a size of about 3 microns or greater per one square centimeter of cured ink coating.
5. A radiation-curable ink composition according to any one of claims 1-4, wherein said ink composition comprises from about 1 to about 20 weight % of said pigment and about 80 to about 90 weight % of a radiation-curable carrier system.
6. A radiation-curable composition according to any one of claims 1-5, wherein said ink composition is adapted to provide a substantially concentric ink coating on a coated optical glass fiber.
7. A method of making a radiation-curable ink composition which when coated and suitably cured on a coated optical glass fiber provides an ink coating having a substantially uniform color, the method comprising the steps of:
- combining a radiation-curable carrier system containing at least one radiation-curable monomer or oligomer with at least one pigment to provide an ink composition, wherein said pigment is present in an amount sufficient to provide a color which is visible without magnification, said pigment being substantially insoluble in said radiation-curable carrier system whereby the particulate shape of said pigment is substantially retained in said radiation-curable carrier system;

filtering said ink composition to selectively remove pigment particles having a size of about 3 microns or greater to substantially avoid pigment induced microbending of an optical glass fiber coated with said ink coating.

- 5
8. A method of making an improved radiation-curable ink composition which when coated and suitably cured on a coated optical glass fiber provides an ink coating having a substantially uniform color, the method
- 10 comprising the steps of:
- combining at least one pigment with at least one monomer or oligomer component of a radiation-curable carrier system to form a colored mixture;
- 15 filtering said colored mixture to selectively remove pigment particles having a size of about 3 microns or greater; and
- combining said filtered colored mixture with remaining components of said radiation-curable carrier system to form a radiation-curable ink
- 20 coating composition which substantially avoids pigment induced microbending of an optical glass fiber coated with said ink coating.
9. A method according to any one of claim 7-8, wherein said filtering step is conducted to provide said
- 25 pigment with about 230 or less particles having a size of about 3 microns or greater per one square centimeter of cured ink coating.
10. A method according to claim 9, wherein said filtering step is conducted to provide said pigment

with about 150 or less particles having a size of about 3 microns or greater per one square centimeter of cured ink coating.

11. A radiation curable ink composition obtainable with
5 the method according to any one of claims 7-10.
12. An ink composition according to claim 11, wherein
said ink composition or said colored mixture is
filtered using a CRK3 filtering unit.
13. A ribbon assembly comprising a plurality of coated
10 optical glass fibers bound together with a matrix
material, wherein at least one of said coated
optical glass fibers comprising:
an optical glass fiber;
an inner primary coating adjacent to said optical
15 glass fiber;
an outer primary coating adjacent to said inner
primary coating; and
an ink coating adjacent to said outer primary
coating; wherein said ink coating is an ink
20 according to any one of claims 1-6 or 11-12.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NL 99/00321

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D11/10 G02B6/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D G02B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 629 285 A (CARTER R SYKES ET AL) 16 December 1986 (1986-12-16) cited in the application ---	1-13
A	WO 97 18493 A (LIGHTGUIDE MATERIALS INC) 22 May 1997 (1997-05-22) page 7, line 11-20 page 19, line 15 - page 20, line 5 ---	1, 5, 13
A	WO 97 19029 A (DSM NV ; JAPAN SYNTHETIC RUBBER CO LTD (NL); ISHIKAWA MIYUKI (JP);) 29 May 1997 (1997-05-29) page 25, line 1-18 page 26, line 26-33 claim 1 --- -/--	1, 13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

Legend: Categories of cited documents

- A document defining the general state of the art which is not considered to be of particular relevance
- 1 earlier document but published on or after the international filing date
- 2 document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another claim or other special reason (as specified)
- 3 document referring to an oral disclosure, use, exhibition or other means
- 4 document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

26 August 1999

Date of mailing of the international search report

06/09/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Miller, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 99/00321

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	<p>EP 0 411 310 A (SUMITOMO ELECTRIC INDUSTRIES) 6 February 1991 (1991-02-06) page 4, line 10-13 page 4, line 18-23 -----</p>	1,13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 99/00321

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4629285	A	16-12-1986	AT 30787 T DE 3560967 A EP 0155092 A JP 60232517 A	15-11-1987 17-12-1987 18-09-1985 19-11-1985
WO 9718493	A	22-05-1997	AU 7554496 A CA 2237393 A EP 0861453 A	05-06-1997 22-05-1997 02-09-1998
WO 9719029	A	29-05-1997	JP 9142889 A AU 7590696 A	03-06-1997 11-06-1997
EP 0411310	A	06-02-1991	AU 622331 B AU 5790290 A DE 69004026 D DE 69004026 T DK 411310 T ES 2047209 T US 5146529 A JP 3087706 A	02-04-1992 03-01-1991 25-11-1993 17-02-1994 07-02-1994 16-02-1994 08-09-1992 12-04-1991

